DEBYE TEMPERATURE OF IONIC CRYSTALS

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ABSTRACT. Relations have been derived connecting the Debye characteristic temperature Θ with some of the lattice properties of the ionic crystals using the interaction potential approach. The relations are independent of the particular shape of the potential functions and also consider the polarization of ions arising from the electric field due to the displacement of the ions. Computed values of Θ agree very well with the Θ values obtained from specific heat and the elastic constant data.

INTRODUCTION

It is well known that the Debye characteristic temperature Θ is an important indicator of a number of physical properties of a solid. The most reliable method of evaluating Θ is from the specific heat of solids. However, when such calorimetric values of Θ are scarce, one has to look for other methods of determining it. Estimates of Θ can be obtained from the elastic constant data (De Launay 1956, Quimby *et al*, 1953, Betts *et al*, 1956a, b, Horton *et al*, 1959, Horton 1959) by finding the sum of the inverse cubes of the three phase velocities of propagation of the elastic waves averaged over all directions. In general, particularly for anisotropic media, the evaluation of this sum is a complicated and tedious problem. Another method which is significantly simple is the computation of Θ utilizing the observed lattice properties of a solid. In the present paper we discuss this approach for ionic crystals of the alkali halide type.

Blackman (1955) from the lattice theory of specific heat obtained a relation between Θ and the compressibility β of a lattice for crystals of the rocksalt type as

$$\Theta = \frac{h}{k} \cdot \frac{1}{2\pi}\left(\frac{5R_0}{m\beta}\right)^{\frac{1}{2}} \qquad (1)$$

where h is Planck's constant, k is the Boltzmann's constant, R_0 is the equilibrium interionic distance and m is the reduced mass. Using a Born-Mayer type of ionic potential Mitra *et al* (1960a) also derived a similar relation. This relation was obtained by considering a specific form of the potential energy of the crystal and the expressions for its first and second derivatives for the static lattices. The characteristic frequency ν was obtained from the relation

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{m}} \qquad \ldots (2)$$

where f is the coefficient of displacement of one lattice relative to the other when the potential energy due to such a relative displacement is expressed as a power series (Huggins 1937). This method ignores the ionic polarization produced by the relative displacement of the two lattices which, however, has a considerable effect on the frequency (Born *et al* 1954). Further, this relation is strictly applicable only if the compressibility and the lattice constants for static lattices are used, which unfortunately are not directly observable. In order to be able to use the room temperature data the relation should be modified. In what follows, relations are derived for ionic crystals connecting the Debye characteristic temperature Θ with the compressibility and other lattice properties but without assuming a specific form of the potential energy function. The electronic polarizability of the ions has also been considered. The relations are further modified to permit the use of the room temperature input data. In addition to the above modifications the present work also differs in the use of more recent experimental data (Cubicciotti 1959) for the compressibility and the interionic distance.

DETERMINATION OF Θ

The potential energy ψ of the crystal per pair of ions can be written in the form

$$\psi = \phi_C + \phi_R \qquad \ldots (3)$$

where ϕ_C is the Coulomb potential and is of the form $\alpha' e^2/R$ where α' is the Madelung's constant. ϕ_R contains the energy contributions other than the electrostatic energy and includes the repulsive energies, the Van der Waals attractive energies and may include the zero-point energy. An expression for the force constant f can be obtained following Born *et al* (1954), Szigeti (1951) and Krishnan *et al* (1951) as

$$f = \frac{1}{3}\left[\, \phi''_R + \frac{2}{R_0}\phi'_R \,\right] \qquad \ldots (4)$$

For static lattices, using the two well known conditions for the first and second derivatives of the potential energy one obtains (Born *et al*, 1954, Szigeti 1951)

$$f = \frac{3cR_0}{\beta} \qquad \ldots (5)$$

where c is the packing factor ($c = 2$ for NaCl type crystals and $c = 1.54$ for CsCl type crystals). In general, using the expressions given by Hildebrand (1931)

$$\left(\frac{d\psi}{dR}\right)_{R=} = \frac{3vT\alpha}{\beta R_0} \qquad \ldots (6)$$

and

$$\left(\frac{d^2\psi}{dR^2}\right)_{R=R} = \frac{9v}{\beta R_0^2} F_{TP} \qquad \ldots (7)$$

where α is the thermal expansion coefficient and F_{TP} is a temperature dependent factor which is very nearly equal to unity (Cubicciotti 1959), we derive for f the expression

$$f = \frac{3cR_0}{\beta}\left[F_{TP} + \frac{2}{3}T\alpha\right] \tag{8}$$

The electronic polarizability is considered by taking into account the contribution to the potential energy from the polarization field of the medium (Born *et al*, 1954) and the expression for ν is obtained as

$$\nu = \frac{1}{2\pi}\left(\frac{\epsilon_\infty+2}{\epsilon+2}\right)^{\frac{1}{2}}\left(\frac{f}{m}\right)^{\frac{1}{2}} \quad \ldots \quad (9)$$

where ϵ and ϵ_∞ are the static and high frequency dielectric constants. In addition, one can also take into account the deformation of the charge distribution resulting from overlap. Lyddane *et al*, (1941) and Szigeti (1951) treat this problem by introducing the idea of an effective charge and obtain another expression connecting the compressibility and the frequency. However as equation (5) is independent of the electronic charge and gives a better agreement with the experiment (Hardy 1961, Hass 1960), it is preferred. Using equations (8) and (9) one can readily obtain

$$\Theta = \frac{F'}{2\pi}\left(\frac{3cR_0}{m\beta}\right)^{\frac{1}{2}} \quad \ldots \quad (10)$$

where

$$F' = \left[\left(F_{TP} + \frac{2}{3}T\alpha\right)\left(\frac{\epsilon_\infty+2}{\epsilon+2}\right)\right]^{\frac{1}{2}} \tag{11}$$

For the simple case when $T = 0$ and the polarization of the medium is ignored one obtains from equation (10), for NaCl type lattices,

$$\Theta = \frac{h}{k}\cdot\frac{1}{2\pi}\left(\frac{6R_0}{m\beta}\right)^{\frac{1}{2}} \quad \ldots \quad (12)$$

which is the same relation as that obtained by Mitra and Joshi (1960a).

RESULTS AND DISCUSSION

Θ calculated from equation (10) using the experimental data for R_0, β (Cubicciotti 1959) and α(Weyl 1955, Kumar 1959, 1960) are given in table 1 (column 2) together with Θ values (column 5) estimated from experimental infrared absorption frequencies (Barnes 1932, Jones *et al*, 1961, Hass 1960). For comparison Θ of Blackman (1955) and θ_D from specific heat data are also given. It is well known now that the Θ values derived from different properties are not

necessarily equal. Θ varies considerably with temperature and as such different Θ values should be compared only if they are evaluated for the same temperature

Table

Values of Debye Temperatures Θ°K

Crystals	Eq. (10)	Exptl. (Blackman 1955)	Exptl. (A.I.P.* 1963)	Exptl. freq.	Elastic constant	(Mitra and Joshi 1960a)	(Blackman 1955)
LiF	399	607—750	732	440[a]	676[d]	834	686
NaF	296	—	—	355[a]	—	469	—
NaCl	250	275—300	321	235[a],235[b]	295[d]	322	292
NaBr	205	—	—	195[c]	202[d]	262	—
NaI	181	—	164	168[c]	156[e]	222	—
KCl	198	218—235	235	205[b],207[c]	230[d]	270	233
KBr	164	152—183	174	167[c]	167[d]	198	185
KI	144	115—200	132	146[c]	124[d]	170	162
RbCl	168	—	—	171[c]	—	203	—
RbBr	125	120—135	—	129[c]	129[e]	148	136
RbI	111	100—118	—	109[c]	102[e]	125	119
CsCl	139	—	—	143[c]	—	166[f]	—
CsBr	103	—	—	106[c]	136[e]	120[f]	—

a Using experimental frequency from Barnes (1932).
b Using experimental frequency from Hass (1960).
c Using experimental frequency from Jones *et al*, (1961).
d Reddy (1963).
e Joshi *et al*, (1960).
f Mitra *et al*, (1960b).
*American Institute of Physics Handbook, 1963.

range. The theory shows that Blackman's relation as well as our relation will not agree with the representative Θ which is obtained from calorimetric measurements in the liquid helium range or lower (column 4). By using the lattice property data at room temperature one expects to get the values of Θ near this temperature. It can be seen from the table that Θ values calculated from equation (10) (column 2) compare well with the Θ values obtained from the room temperature elastic constant data (column 6) and with the Θ values from experimental values of frequencies (column 5) and exhibit a significant improvement over the earlier computed values (columns 7 and 8) using equations similar to ours. When a reference is made to the θ_D-Tplots for alkali halides (Blackman 1955) it is to be noted that our values are lower than the average values of θ_D for LiF and NaCl. For KCl the curve indicates a trend to lower values when approaching temperatures of the order of 275°K and as such our value exhibits a reasonable agreement.

It also applies to KBr. For KI, even though our value compares well with the average θ_D, it does not agree with the general tendency of θ_D value to increase with increasing temperature. Blackman also points out that the case of KI is anomalous and further investigation of this crystal is desirable. For RbBr and RbI our values agree well with the average θ_D values. For CsCl and CsBr only indirect experimental values of Θ from frequency are available and with these our values show an excellent agreement. In general for most of the ionic crystals our equation (10) seems to be definitely superior.

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